**Dual Activation in Asymmetric Allylsilane Addition to Chiral *N*-Acylhydrazones:
Method Development, Mechanistic Studies, and
Elaboration of Homoallylic Amine Adducts**

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Materials and Methods. Reactions employed oven- or flame-dried glassware under nitrogen unless otherwise noted. THF and toluene were distilled from sodium/benzophenone ketyl under argon. CH_2Cl_2 was distilled from CaH_2 under argon or nitrogen. Nitrogen was passed successively through columns of anhydrous CaSO_4 and R3-11 catalyst for removal of water and oxygen, respectively. All other materials were used as received from commercial sources unless otherwise noted. Tetrabutylammonium triphenyldifluorosilicate (TBAT) was prepared according to literature methods,¹ or commercial TBAT was recrystallized from EtOAc. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator. Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in the initial elution solvent. Gradient flash chromatography was conducted by adsorption of product mixtures on silica gel, packing over a short pad of clean silica gel as a slurry in hexane, and eluting with a continuous gradient from hexane to the indicated solvent. Radial chromatography refers to centrifugally accelerated thin-layer chromatography performed with a Chromatotron using commercially supplied rotors. Melting points are uncorrected. Nuclear magnetic resonance (NMR) data were obtained at operating frequencies of 500 or 300 MHz for ^1H and 125 or 75 MHz for ^{13}C . Infrared spectra were recorded using a single beam FT-IR spectrophotometer by standard transmission methods or by use of an attenuated total reflectance (ATR) probe. Optical rotations were determined using a digital polarimeter operating at ambient temperature. Low resolution mass spectra were obtained using sample introduction by dip, liquid chromatography or gas chromatography. High resolution mass spectra and combustion analyses were obtained from external commercial and institutional services. Chromatographic diastereomer ratio analyses employed GCMS with 15 mL x 0.25 mm I.D X 0.25 μ F.T 5%-phenyl-95%-dimethylsiloxane column and helium as mobile phase or HPLC with Microsorb-MV Si 8um 100A or Chiralcel OD columns (2-propanol/hexane as mobile phase) or Chirex 3014 column (chloroform/hexane as mobile phase).

Note regarding specific optical rotations: Several specific rotations $[\alpha]_D$ of compounds **1b–1f**, **2a–2f**, and **4** were recorded erroneously in the supporting information of the preliminary report.² Corrected $[\alpha]_D$ data are reported herein.

Preparation of enantiopure *N*-acylhydrazones (General Procedure A): A procedure based on the literature method³ was employed. To a solution of (*S*)-3-amino-4-phenylmethyl-2-oxazolidinone (0.1–0.3 mmol) in toluene (10 mL) was added MgSO_4 (200 mg), a catalytic amount of *p*-TsOH (ca. 5 mol%) and aldehyde (ca. 1.5 equiv). After heating at reflux for 10 min, concentration and flash chromatography (5:1 hexane/ethyl acetate) gave pure hydrazones **1a–1h**.

(*S*)-3-(Benzylidene)amino-4-phenylmethyl-2-oxazolidinone (1a). From (*S*)-3-amino-4-phenylmethyl-2-oxazolidinone (60 mg, 0.31 mmol) and benzaldehyde (0.05 mL, 0.49 mmol) by General Procedure A was obtained **1a** (70 mg, 81%) as a colorless solid, the properties of which matched the published data.⁴

(*S*)-3-(*p*-Methylbenzylidene)-amino-4-phenylmethyl-2-oxazolidinone (1b).

From (*S*)-3-amino-4-phenylmethyl-2-oxazolidinone (43 mg, 0.22 mmol) and *p*-tolualdehyde (0.04 mL, 0.34 mmol) by General Procedure A was obtained **1b** (62 mg, 94%) as a colorless solid; mp 111–112 °C; $[\alpha]_D^{20}$ -22° (c 0.11, CHCl_3); IR (film) 3027, 2918, 1760, 1615, 1497, 1474, 1455, 1403, 1212, 1089 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.87 (s, 1H), 7.63–7.04 (m, 9H), 4.50–4.43 (m, 1H), 4.28 (dd, J = 8.0, 8.0 Hz, 1H), 4.12 (dd, J = 8.8, 5.6 Hz, 1H), 3.30 (dd, J = 13.9, 3.6 Hz, 1H), 2.90 (dd, J = 13.9, 8.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.9, 151.2, 140.8, 135.5, 131.8, 129.5, 129.4, 128.9, 127.5, 127.3,

65.8, 58.4, 37.8, 21.5; MS (CI) m/z (relative intensity) 295 ($[M+H]^+$, 100%); Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.31; H, 6.25; N, 9.25.

(S)-3-(3'-Nitrobenzylidene)amino-4-phenylmethyl-2-oxazolidinone (1c).

From (S)-3-amino-4-phenylmethyl-2-oxazolidinone (50 mg, 0.26 mmol) and *m*-nitrobenzaldehyde (0.06 mL, 0.40 mmol) by General Procedure A was obtained **1c** (75 mg, 91%) as a colorless solid; mp 148–150 °C; $[\alpha]_D^{23}$ -5.5° (*c* 0.29, $CHCl_3$); IR (film) 3057, 2921, 1754, 1534, 1399, 1352, 1266, 1099 cm^{-1} ; ^1H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.51 (s, 1H), 8.21 (dddd, $J = 8.2, 1.0, 1.0, 1.0$ Hz, 1H), 7.98 (dd, $J = 7.7, 0.9$ Hz, 1H), 7.57 (dd, $J = 7.7, 7.7$ Hz, 1H), 7.34–7.16 (m, 5H), 4.58–4.53 (m, 1H), 4.36 (dd, $J = 8.1, 8.1$ Hz, 1H), 4.17 (dd, $J = 8.2, 5.6$ Hz, 1H), 3.32 (dd, $J = 13.9, 4.1$ Hz, 1H), 2.95 (dd, $J = 13.9, 8.4$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 148.8, 136.5, 135.1, 133.0, 129.7, 129.4, 129.0, 127.4, 124.6, 121.7, 66.0, 58.6, 38.2; MS (EI) m/z (relative intensity) 325 (M^+ , 29%); Anal. Calcd. for $C_{17}H_{15}N_3O_4$: C, 62.76; H, 4.65; N, 12.92. Found: C, 62.64; H, 4.77; N, 12.72.

(S)-3-(2'-Naphthylidene)-amino-4-phenylmethyl-2-oxazolidinone (1d).

From (S)-3-amino-4-phenylmethyl-2-oxazolidinone (43 mg, 0.22 mmol) and 2-naphthaldehyde (52 mg, 0.33 mmol) by General Procedure A was obtained **1d** (67 mg, 92%) as a colorless solid; mp 147–148 °C; $[\alpha]_D^{20}$ -38° (*c* 0.12, $CHCl_3$); IR (film) 3027, 2918, 2850, 1752, 1651, 1456, 1397, 1265, 1222, 1093 cm^{-1} ; ^1H NMR (500 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.02–7.17 (m, 12H), 4.53–4.45 (m, 1H), 4.35 (dd, $J = 8.7, 8.7$ Hz, 1H), 4.19 (dd, $J = 8.8, 5.5$ Hz, 1H), 3.38 (dd, $J = 13.9, 3.8$ Hz, 1H), 2.92 (dd, $J = 13.9, 8.7$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 150.5, 135.4, 134.5, 133.2, 132.1, 129.6, 129.4, 129.0, 127.5, 128.6, 127.9, 127.3, 127.2, 126.7, 122.8, 65.8, 58.2, 37.7; MS (CI) m/z (relative intensity) 330 (M^+ , 25%); Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.63; H, 5.50; N, 8.47.

(S)-3-(2'-Furanylidene)amino-4-phenylmethyl-2-oxazolidinone (1e).

From (S)-3-amino-4-phenylmethyl-2-oxazolidinone (48 mg, 0.25 mmol) and 2-furaldehyde (0.06 mL, 0.41 mmol) by General Procedure A was obtained **1e** (62 mg, 92%) as an air- and light-sensitive pale yellow oil; $[\alpha]_D^{20}$ -65° (*c* 0.06, $CHCl_3$); IR (film) 3028, 2917, 2849, 1751, 1715, 1456, 1399, 1266, 1224, 1095 cm^{-1} ; ^1H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.55 (d, $J = 1.7$ Hz, 1H), 7.34–7.19 (m, 5H), 6.78 (dd, $J = 3.4, 0.9$ Hz, 1H), 6.56 (dd, $J = 3.4, 1.7$ Hz, 1H), 4.49–4.45 (m, 1H), 4.29 (dd, $J = 8.2, 8.2$ Hz, 1H), 4.12 (dd, $J = 8.9, 5.9$ Hz, 1H), 3.35 (dd, $J = 13.9, 3.7$ Hz, 1H), 2.92 (dd, $J = 13.9, 8.9$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 149.7, 144.8, 141.3, 135.2, 129.4, 128.9, 127.3, 114.3, 111.9, 65.7, 58.8, 37.9; MS (CI) m/z (relative intensity) 295 ($[M+H]^+$, 100%); HRMS (FAB) m/z : $[M+H]^+$ calcd. for $C_{15}H_{15}N_2O_3$ 271.1083; found, 271.1066.

(S)-3-(*trans*-Cinnamylidene)amino-4-phenylmethyl-2-oxazolidinone (1f).

From (S)-3-amino-4-phenylmethyl-2-oxazolidinone (48 mg, 0.25 mmol) and *trans*-cinnamaldehyde (0.05 mL, 0.40 mmol) by General Procedure A was obtained **1f** (74 mg, 97%) as a colorless solid; mp 88–90 °C; $[\alpha]_D^{20}$ -71° (*c* 0.08, $CHCl_3$); IR (film) 3055, 2919, 2850, 1751, 1713, 1627, 1451, 1400, 1266, 1214, 1091 cm^{-1} ; ^1H NMR (500 MHz, $CDCl_3$) δ 8.55 (dd, $J = 7.9, 7.9$ Hz, 1H), 7.50 (dd, $J = 1.5, 1.5$ Hz, 2H), 7.47–6.96 (m, 10H), 4.47–4.42 (m, 1H), 4.27 (dd, $J = 8.8, 8.8$ Hz, 1H), 4.14 (dd, $J = 8.8, 5.1$ Hz, 1H), 3.26 (dd, $J = 13.9, 3.3$ Hz, 1H), 2.92 (dd, $J = 13.9, 8.8$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 151.2, 140.8, 135.6, 131.8, 129.5, 129.4, 128.9, 127.5, 127.3, 65.8, 58.4, 37.8; MS (CI) m/z (relative intensity) 306 (M^+ , 25%).

(S)-3-(Propylidene)amino-4-phenylmethyl-2-oxazolidinone (1g). From (*S*)-3-amino-4-phenylmethyl-2-oxazolidinone (27 mg, 0.14 mmol) and propionaldehyde (0.02 mL, 0.27 mmol) by General Procedure A was obtained **1g** (30 mg, 92%) as colorless oil.⁴

(S)-3-(3,4-Dimethoxybenzylidene)amino-4-phenylmethyl-2-oxazolidinone (1h). From (*S*)-3-amino-4-phenylmethyl-2-oxazolidinone (600 mg, 3.1 mmol) and veratraldehyde (570 mg, 3.4 mmol) by General Procedure A was obtained **1h** (1.0 g, 98%) as a colorless solid; mp 113–115 °C; $[\alpha]_D^{23}$ -56.1° (*c* 0.18, CHCl₃); IR (film) 2922, 2851, 1764, 1601, 1514, 1457, 1403, 1267, 1218, 1139, 1089, 1023 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.75 (s, 1H), 7.34–7.13 (m, 7H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.48–4.45 (m, 1H), 4.28 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.11 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.28 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.90 (dd, *J* = 13.5, 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 154.0, 151.4, 149.5, 135.5, 129.4, 128.9, 127.4, 127.2, 122.5, 110.8, 108.5, 65.8, 58.4, 56.0 (2C), 37.8; MS (EI) *m/z* (relative intensity) 325 (M⁺, 29%); Anal. Calcd. for C₁₉H₂₀N₂O₄: C, 67.05; H, 5.92; N, 8.23. Found: C, 66.90; H, 5.86; N, 8.12.

Allyl Addition to Hydrazones: General Procedures B–D

Addition using allyltrimethylsilane and TBAF (General Procedure B): To a mixture of hydrazone (0.3 mmol), allyltrimethylsilane (0.36 mmol) and 4 Å molecular sieves in THF (2 mL) was added TBAF (30 μ L, 1.0 M in THF, 0.03 mmol). The reaction mixture was stirred for 20 h, and filtered on a short silica gel column. The filtrate was concentrated and chromatographed (4:1 hexane/ethyl acetate) to give pure hydrazines **2a**.

Addition using allylmagnesium bromide (General Procedure C): A mixture of hydrazone (0.2 mmol) and indium triflate (0.26 mmol) in CH₂Cl₂ (2.2 mL) was stirred at room temperature for 2 h. Then, allylmagnesium bromide (0.6 mL, 1.0 M in Et₂O, 0.6 mmol) was added dropwise. After 2 d, the reaction was quenched by 0.5% HCl solution. The organic phase was separated, dried over MgSO₄, and purified by flash chromatography to give pure hydrazines **2**.

Addition using tetraallylsilane and TBAT (General Procedure D): A mixture of hydrazone (0.2 mmol) and indium triflate (0.26 mmol) in CH₂Cl₂ (2.2 mL) was stirred at room temperature. Meanwhile, a mixture of TBAT (0.6 mmol) and tetraallylsilane (0.6 mmol) in CH₂Cl₂ (0.8 mL) was stirred in another flask. After 4 h, the TBAT mixture was added to the hydrazone mixture. After 2 d, 2 mL of water was added. The organic phase was separated, dried over MgSO₄, concentrated and purified by flash chromatography to give pure hydrazines **2a**. Diastereomeric ratios were determined by HPLC (MICROSORB-MV^{TM} C8 column, eluted with 95:5 hexane/isopropanol) in comparison with authentic mixtures (dr ca. 5:1) obtained in less selective addition reactions (i.e., by General Procedure C). One example is given below for the minor diastereomer of **2a**; other minor diastereomers were not separated in quantities sufficient for full characterization.

(4*S*,1'*S*)-3-(1'-Allyl-1'-phenylmethyl-amino)-4-phenylmethyl-2-oxazolidinone (2a). From **1a** (56 mg, 0.2 mmol) by General Procedure D was obtained **2a** (50 mg, 78%) as a colorless oil; $[\alpha]_D^{23}$ -19.5° (*c* 0.43, CHCl₃); IR (film) 3290, 3028, 2927, 1754, 1699, 1653, 1558, 1497, 1456, 1399, 1093, 918 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.39–7.13 (m, 8H), 6.91 (dd, *J* = 7.2 Hz, 2H), 5.74 (dddd, *J* = 10.2, 10.2, 7.8, 6.1 Hz, 1H), 5.13 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.05 (dd, *J* = 10.3, 1.0 Hz, 1H), 4.43 (s, 1H), 4.23 (ddd,

$J = 7.9, 1.3, 1.3$ Hz, 1H), 3.77-3.70 (m, 2H), 3.16 (dd, $J = 13.4, 3.4$ Hz, 1H), 3.06-3.04 (m, 1H), 2.45-2.40 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.7, 142.1, 135.99, 135.98, 134.2, 129.1, 128.8, 128.5, 127.98, 127.93, 126.9, 118.4, 65.8, 62.9, 58.2, 40.3, 36.8; MS (EI) m/z (relative intensity) 323 ($[\text{M}+\text{H}]^+$, 40%); Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2$: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.40; H, 6.89; N, 8.59.

(4S,1'R)-3-(1'-Allyl-1'-phenylmethyl-amino)-4-phenylmethyl-2-

oxazolidinone ((1'R)-2a). From **1a** (84 mg, 0.30 mmol) by General Procedure B was obtained **2a** (54 mg, 56%) as a mixture of diastereomers ((1'S):(1'R) = 5:1), along with unreacted **1a** (25 mg, 30%). From a larger scale run (302 mg of **1a**, 1.08 mmol) was obtained a mixture of (1'S)-**2a** and (1'R)-**2a** (107 mg, 33%). Fractions enriched

in the minor diastereomer were pooled and further flash chromatography afforded pure (1'R)-**2a** (10 mg, 3%) as a colorless solid. mp 63–64 °C; $[\alpha]_D^{20} +60^\circ$ (c 0.08, CHCl_3); IR (film) 3277, 3030, 2916, 1759, 1699, 1653, 1559, 1507, 1457, 1091 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.22 (m, 8H), 7.02 (dd, $J = 7.4$ Hz, 2H), 5.79 (dddd, $J = 10.3, 10.3, 6.5, 6.5$ Hz, 1H), 5.14 (dd, $J = 17.0, 1.4$ Hz, 1H), 5.07 (dd, $J = 10.2$ Hz, 1H), 4.38 (d, $J = 1.5$ Hz, 1H), 4.30 (ddd, $J = 6.9, 1.5, 1.5$ Hz, 1H), 4.02 (dd, $J = 7.8, 7.6$ Hz, 1H), 3.87-3.80 (m, 2H), 2.95 (dd, $J = 13.8, 3.5$ Hz, 1H), 2.58-2.53 (dd, $J = 7.9, 7.7$ Hz, 2H), 2.00 (dd, $J = 10.3, 9.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0, 140.9, 136.1, 134.6, 134.2, 129.1, 128.9, 128.5, 128.4, 127.98, 126.98, 118.1, 66.5, 62.9, 59.4, 39.4, 37.4; MS (EI) m/z (relative intensity) 281 ($[\text{M-allyl}]^+$, 100%); Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2$: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.70; H, 7.08; N, 8.43.

(4S,1'S)-3-(1'-Allyl-1'-(4''-methyl)-phenylmethyl-amino)-4-phenylmethyl-2-

oxazolidinone (2b). From **1b** (59 mg, 0.20 mmol) by General Procedure D was obtained **2b** (63 mg, 94%) as a colorless oil; $[\alpha]_D^{20} -27^\circ$ (c 0.1, CHCl_3); IR (film) 3286, 3026, 2918, 1757, 1638, 1604, 1497, 1454, 1237, 1092, 918 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33-7.17 (m, 8H), 7.00 (dd, $J = 7.0, 7.0$ Hz, 2H), 5.82 (dddd, $J = 17.3, 10.3, 7.7, 6.1$ Hz, 1H), 5.20 (dd, $J = 17.1, 1.4$ Hz, 1H), 5.12 (dd, $J = 10.2, 1.8$ Hz, 1H), 4.47 (s, 1H), 4.26 (dd, $J = 7.0, 7.0$ Hz, 1H), 3.83-3.81 (m, 2H), 3.22 (dd, $J = 13.3, 3.3$ Hz, 1H), 3.19-3.16 (m, 1H), 2.52-2.45 (m, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.8, 139.0, 137.6, 136.2, 134.4, 129.3, 128.9, 127.9, 127.0, 118.4, 65.8, 62.6, 58.3, 40.4, 36.7, 21.3; MS (CI) m/z (relative intensity) 337 ($[\text{M}+\text{H}]^+$, 4%).

(4S,1'S)-3-(1'-Allyl-1'-(3''-nitro)phenylmethyl-amino)-4-phenylmethyl-2-

oxazolidinone (2c). From **1c** (80 mg, 0.25 mmol) by General Procedure D was obtained **2c** (64 mg, 71%) as a colorless solid; mp 47–48 °C; $[\alpha]_D^{23} -46^\circ$ (c 0.31, CHCl_3); IR (film) 3291, 3064, 2917, 1756, 1642, 1531, 1351, 1267, 1096, 1002 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.39 (s, 1H), 8.16 (ddd, $J = 2.2, 2.2, 1.2$ Hz, 1H), 7.68-7.05 (m, 7H), 5.78 (dddd, $J = 10.1, 10.1, 7.9, 6.2$ Hz, 1H), 5.12-5.04 (m, 2H), 4.52 (s, 1H), 4.46 (dd, $J = 7.5, 7.5$ Hz, 1H), 3.91 (dd, $J = 9.0, 4.0$ Hz, 1H), 3.76-3.70 (m, 1H), 3.19-3.11 (m, 2H), 2.57 (dd, $J = 13.0, 9.6$ Hz, 1H), 2.38-2.28 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.9, 144.6, 135.6, 134.3, 133.1, 129.5, 129.2, 129.0, 127.2, 122.9, 122.4, 119.4, 65.8, 62.4, 58.9, 40.6, 36.9; MS (EI) m/z (relative intensity) 368 ($[\text{M}+\text{H}]^+$, 42%); Anal. Calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_4$: C, 65.38; H, 5.76; N, 11.44. Found: C, 65.31; H, 5.79; N, 11.33.

(4S,1'S)-3-(1'-Allyl-1'-naphthyl-methyl-amino)-4-phenylmethyl-2-

oxazolidinone (2d). From **1d** (68 mg, 0.20 mmol) by General Procedure D was obtained **2d** (61 mg, 82%) as a colorless oil; $[\alpha]_D^{23} -58.8^\circ$ (*c* 0.17, CHCl₃); IR (film) 3286, 3059, 3027, 2917, 1755, 1638, 1497, 1403, 1220, 1093 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.97-6.94 (m, 12H), 5.82 (dddd, *J* = 10.2, 10.2, 8.6, 6.0 Hz, 1H), 5.21 (dddd, *J* = 17.0, 1.5, 1.4, 1.5 Hz, 1H), 5.13 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.57 (dd, *J* = 1.4, 1.4 Hz, 1H), 4.47 (ddd, *J* = 7.9, 7.9, 1.3 Hz, 1H), 3.78 (dd, *J* = 8.9, 4.3 Hz, 1H), 3.69 (dd, *J* = 8.8, 7.9 Hz, 1H), 3.25 (dd, *J* = 13.4, 3.3 Hz, 1H), 3.07 (dddd, *J* = 13.7, 7.7, 3.9, 3.9 Hz, 1H), 2.58-2.48 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.8, 139.5, 135.91, 135.9, 134.1, 133.3, 133.2, 129.1, 128.8, 128.4, 127.9, 127.8, 127.4, 126.9, 126.4, 126.1, 125.3, 118.6, 65.7, 63.0, 58.3, 40.4, 36.8; MS (EI) *m/z* (relative intensity) 372 ([M+H]⁺, 4%); Anal. Calcd. for C₂₄H₂₄N₂O₂: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.07; H, 6.81; N, 7.18.

(4S,1'S)-3-(1'-Allyl-1'-furanyl-methyl-amino)-4-phenylmethyl-2-oxazolidinone

(2e). From **1e** (60 mg, 0.20 mmol) by General Procedure D was obtained **2e** (36 mg, 58%) as a colorless oil; $[\alpha]_D^{20} -13^\circ$ (*c* 0.1, CHCl₃); IR (film) 3286, 3064, 3028, 2917, 1756, 1643, 1558, 1497, 1406, 1239, 1094 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.44-7.04 (m, 6H), 6.35 (dd, *J* = 3.2, 2.2 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.5 Hz, 1H), 5.77 (dddd, *J* = 10.2, 10.2, 7.8, 6.1 Hz, 1H), 5.20 (dddd, *J* = 17.1, 1.4, 1.4, 1.4 Hz, 1H), 5.13 (dd, *J* = 9.8, 0.6 Hz, 1H), 4.41-4.38 (m, 2H), 3.97-3.89 (m, 2H), 3.22 (dddd, *J* = 15.7, 3.8, 3.8, 3.8 Hz, 1H), 2.62-2.55 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 157.7, 154.1, 142.3, 135.9, 133.7, 129.3, 128.9, 126.9, 118.5, 110.6, 108.5, 66.1, 58.3, 56.0, 36.9; MS (CI) *m/z* (relative intensity) 313 ([M+H]⁺, 0.8%); Anal. Calcd. for C₁₈H₂₀N₂O₃: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.39; H, 6.54; N, 8.75.

(4S,1'S)-3-(1'-Allyl-1'-trans-cinnamyl-methyl-amino)-4-phenylmethyl-2-

oxazolidinone (2f). From **1f** (66 mg, 0.22 mmol) by General Procedure D was obtained **2f** (45 mg, 60%) as a colorless oil; $[\alpha]_D^{23} -48.7^\circ$ (*c* 0.11, CHCl₃); IR (film) 3288, 3060, 3029, 2917, 1755, 1639, 1495, 1403, 1266, 1093, 970 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.25 (m, 8H), 7.12 (dd, *J* = 7.9 Hz, 2H), 6.56 (dd, *J* = 15.8 Hz, 1H), 6.09 (ddd, *J* = 15.9, 8.7, 1.2 Hz, 1H), 5.86 (dddd, *J* = 17.3, 10.4, 7.0, 7.0 Hz, 1H), 5.21 (ddd, *J* = 2.9, 2.9, 1.4 Hz, 1H), 5.15 (dd, *J* = 10.3 Hz, 1H), 4.28 (s, 1H), 4.05 (dd, *J* = 7.7, 7.7 Hz, 1H), 3.96-3.89 (m, 3H), 3.29 (dd, *J* = 13.5, 3.6 Hz, 1H), 2.65 (dd, *J* = 13.8, 9.5 Hz, 1H), 2.36 (dd, *J* = 6.8, 5.8 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 157.9, 136.8, 135.9, 133.9, 133.3, 130.3, 129.3, 128.9, 128.8, 127.8, 127.1, 126.6, 118.3, 66.0, 61.7, 59.5, 38.5, 37.3; MS (CI) *m/z* (relative intensity) 349 ([M+H]⁺, 3%); Anal. Calcd. for C₂₂H₂₄N₂O₂: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.61; H, 6.95; N, 7.97.

(4S, 3R)-3-(5'-Hexen-3'-yl)amino)-4-phenylmethyl-2-oxazolidinone (2g).

From **1g** (50 mg, 0.20 mmol) by General Procedure D was obtained **2g** (28 mg, 51%, dr 82:18) as a colorless oil; IR (film) 3290, 3028, 2965, 2918, 1759, 1637, 1497, 1455, 1399, 1217, 1090 cm⁻¹; Major diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.13 (m, 5H), 5.88 (dddd, *J* = 10.2, 10.2, 7.8, 6.2 Hz, 1H), 5.18 (ddd, *J* = 17.1, 3.4, 1.6 Hz), 5.13 (dd, *J* = 6.5, 1.2 Hz, 1H), 4.13 (dd, *J* = 8.9, 4.5 Hz, 1H), 4.00-3.98 (m, 1H), 3.95-3.86 (m, 2H), 3.30 (ddd, *J* = 13.1, 3.4, 3.4 Hz, 1H), 2.30-2.21 (m, 3H), 1.51-1.48 (m, 2H), 0.98-0.90 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 158.4, 136.1, 135.0, 129.1, 128.9, 127.1, 117.6, 65.9, 65.7, 59.7, 59.3, 37.2, 36.3, 24.9, 9.3; MS (EI) *m/z* (relative intensity) 274 (M⁺, 0.9%); Anal. Calcd. for C₁₆H₂₂N₂O₂: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.66; H, 8.11; N, 10.16.

(4S,1'S)-3-(1'-(3,4-Dimethoxyphenyl)but-3'-enylamino)-4-phenylmethyl-2-oxazolidinone (2h). From **1h** (1.53 g, 4.5 mmol) by General Procedure D, using $\text{In}(\text{OTf})_3$ from Alfa Aesar, was obtained **2h** (920 mg, dr 96:4, 54% yield) as a colorless oil. Major diastereomer (1'S)-**2h**: $[\alpha]_D^{23} -75^\circ$ (c 0.08, CHCl_3); IR (film) 3286, 2934, 2835, 1753, 1593, 1516, 1455, 1262, 1237, 1141, 1092 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.25-7.18 (m, 7H), 6.83 (d, $J = 8.1$ Hz, 1H), 5.81-5.75 (m, 1H), 5.17 (d, $J = 17.0$ Hz, 1H), 5.10 (d, $J = 10.2$ Hz, 1H), 4.45 (br s, 1H), 4.24 (dd, $J = 7.1, 7.1$ Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.80-3.79 (m, 2H), 3.21-3.15 (m, 2H), 2.51 (dd, $J = 13.1, 9.5$ Hz, 1H), 2.46-2.43 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.6, 149.1, 148.7, 135.9, 134.5, 134.3, 129.0, 128.8, 126.9, 120.3, 118.3, 111.1, 110.8, 65.8, 62.4, 58.1, 56.0, 55.9, 40.3, 36.8; MS (APCI) m/z (relative intensity) 383 ($[\text{M}+\text{H}]^+$, 7%); Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$: C, 69.10; H, 6.85; N, 7.32. Found: C, 68.91; H, 6.75; N, 7.30. Minor diastereomer (1'R)-**2h**: Colorless oil; $[\alpha]_D^{23} +28^\circ$ (c 0.1, CHCl_3); IR (film) 3281, 2934, 2836, 1754, 1593, 1516, 1455, 1419, 1263, 1141, 1092, 1027 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.27-7.03 (m, 5H), 6.95 (d, $J = 1.9$ Hz, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 6.80 (d, $J = 8.2$ Hz, 1H), 5.71 (dddd, $J = 16.3, 13.8, 7.3, 6.1$ Hz, 1H), 5.14-5.12 (m, 1H), 5.07-5.02 (m, 1H), 4.40-4.25 (br, 1H), 4.20 (dd, $J = 7.0, 7.0$ Hz, 1H), 4.01 (dd, $J = 7.3, 7.3$ Hz, 1H), 3.88-3.82 (m, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 3.00 (dd, $J = 13.9, 3.8$ Hz, 1H), 2.52-2.43 (m, 2H), 2.14 (dd, $J = 13.0, 10.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.7, 149.0, 148.8, 136.0, 134.6, 133.4, 128.9, 128.8, 127.0, 120.5, 117.9, 111.3, 111.0, 66.4, 62.5, 58.9, 56.0, 55.9, 39.7, 37.6; MS (APCI) m/z (relative intensity) 341 ($[\text{M}-\text{allyl}]^+$, 100%); Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4$: C, 69.10; H, 6.85; N, 7.32. Found: C, 68.83; H, 6.84; N, 7.08.

Trifluoroacetyl-mediated N-N bond cleavage with SmI_2 (General Procedure E): To a solution of the hydrazone in THF (0.1 M) at -78°C was added $n\text{-BuLi}$ (1.6 M in hexane, 1.1 equiv). After 40 min, freshly distilled trifluoroacetic anhydride (1.8 equiv) was added and the mixture was allowed to warm to ambient temperature over 16 h. Concentration and flash chromatography gave the trifluoroacetamide. To a solution of the trifluoroacetamide in MeOH (0.5 M), was added SmI_2 (0.3 M in THF, 8 equiv) dropwise under N_2 via a syringe. After 30 min, the dark blue solution was opened to air, and the color changed to yellow. Concentration and flash chromatography gave the amide products and recovered auxiliary where applicable. Note the concentration of SmI_2 was assumed on the basis of preparation; the actual concentration is likely lower than 0.3 M. Use of a freshly titrated SmI_2 solution (0.1 M) showed a 3:1 molar ratio of SmI_2 :substrate was sufficient to achieve complete conversion in 5 min.

(S)-2,2,2-Trifluoro-N-(1-phenyl-but-3-enyl)-acetamide (6a). From **2a** (10 mg, 0.03 mmol) by General Procedure E was obtained the *N*-TFA derivative (11 mg, 85%) as colorless oil; IR (film) 1795, 1713, 1702, 1650 cm^{-1} ; MS (APCI) m/z (relative intensity) 419 ($[\text{M}+1]^+$, 57%). Treatment of this trifluoroacetamide (17 mg, 0.041 mmol) with SmI_2 by General Procedure E was obtained **6a** (9.4 mg, 95%) as colorless solid: mp $70\text{--}72^\circ\text{C}$; $[\alpha]_D^{25} -102^\circ$ (c 0.9, CHCl_3); IR (film) 3343, 3080, 2950, 2924, 2857, 1696, 1543, 1176, 926 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.24 (m, 5H), 6.57 (br, 1H), 5.67 (dddd, $J = 17.5, 10.5, 7.5, 7.5$ Hz, 1H), 5.17-5.12 (m, 2H), 5.07 (dddd, apparent quintet, $J = 7.0$ Hz, 1H), 2.64 (dd, $J = 6.9, 6.9$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.5 (d, $^2J_{\text{CF}} = 36.9$ Hz), 139.5, 132.8, 128.9, 128.1, 126.4, 119.3, 115.9 (d, $^1J_{\text{CF}} = 286.4$ Hz), 53.2, 39.9; MS (CI) m/z (relative intensity) 244 ($[\text{M}+\text{H}]^+$, 3%); Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{F}_3\text{NO}$: C, 59.26; H, 4.97; N, 5.76. Found: C, 59.24; H, 4.94; N, 5.61.

***N*-[1-(3,4-Dimethoxy-phenyl)-but-3-enyl]-2,2,2-trifluoroacetamide (6h).** From **2h** (0.907 g, 2.37 mmol) by General Procedure E was obtained the *N*-TFA derivative (1.01 g, 89%) as colorless oil; IR (film) 1795,

1714, 1700, 1649 cm^{-1} ; MS (CI) m/z (relative intensity) 479 ($[\text{M}+1]^+$, 18%). Treatment of this trifluoroacetamide (964 mg, 2.0 mmol) with SmI_2 by General Procedure E was obtained (*S*)-**6h** (575 mg, 94%) as colorless solid; $[\alpha]_{\text{D}}^{25} -64^\circ$ (c 0.17, CHCl_3). This compound was spectroscopically (^1H and ^{13}C NMR) identical to a racemic sample prepared from **27**⁵ (159 mg, 0.489 mmol) by treatment with SmI_2 as described within General Procedure E, giving amine *rac*-**7** (96 mg, 97%) as a colorless solid. To a solution of *rac*-**7** (0.20 g, 0.966 mmol) in anhydrous CH_2Cl_2 (3 mL) was added $(\text{CF}_3\text{CO})_2\text{O}$ (redistilled, 0.28 mL, 1.96 mmol) dropwise via syringe. After ca. 16 h, the resulting yellow mixture was directly submitted to flash chromatography (2:1 hexane/EtOAc) to give *rac*-**6h** (276 mg, 95%) as a colorless solid; mp 54–56 $^\circ\text{C}$; IR (film) 3305, 3082, 2938, 2839, 1700, 1518, 1266, 1183, 1161, 1027 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.84–6.80 (m, 2H), 6.76 (s, 1H), 6.45 (br d, $J = 5.9$ Hz, 1H), 5.67 (dddd, $J = 17.1, 10.2, 7.0, 7.0$ Hz, 1H), 5.17–5.11 (m, 2H), 5.00 (ddd, $J = 7.1, 7.1, 7.1$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.62 (dd, $J = 7.0, 7.0$ Hz, 2H); ^{13}C NMR (125 MHz, CHCl_3) δ 156.4 ($^2J_{\text{CF}} = 36.9$ Hz), 149.4, 149.0, 133.0, 132.0, 119.0, 118.5, 115.9 (d, $^1J_{\text{CF}} = 286.5$ Hz), 111.5, 110.2, 56.0 (2C), 53.1, 39.7; ^{13}C NMR (125 MHz, toluene- d_8) δ 156.0 (d, $^2J_{\text{CF}} = 46.4$ Hz), 150.1, 149.7, 133.5, 132.3, 118.5, 118.1, 116.4 ($^1J_{\text{CF}} = 285.3$ Hz), 112.2, 111.1, 55.4, 55.3, 53.0, 39.3; MS (APCI) m/z (relative intensity) 304 ($[\text{M}+\text{H}]^+$, 6%); Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{F}_3\text{NO}$: C, 55.44; H, 5.32; N, 4.62. Found: C, 55.55; H, 5.36; N, 4.70.

(S)-1-(3,4-Dimethoxyphenyl)-but-3-enylamine (7). To a solution of **6h** (0.18 g,

0.594 mmol) in $\text{MeOH}/\text{H}_2\text{O}$ (6 mL, 5:1), was added K_2CO_3 (0.82 g, 5.88 mmol).

After heating at reflux for 3 h, the mixture was concentrated and the residue was partitioned between EtOAc and water. The organic phase was washed with brine, dried over MgSO_4 and concentrated to give **7** (112 mg, 91%) as pale yellow needles; mp 55–56 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} -13.6^\circ$ (c 0.5, CHCl_3); IR (film) 3374, 3069, 2933, 2834, 1677, 1592, 1514, 1462, 1417, 1262, 1232, 1139, 1028 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.90–6.80 (m, 3H), 5.74 (dddd, $J = 18.1, 10.2, 8.0, 6.2$ Hz, 1H), 5.08 (dd, $J = 17.0, 1.3$ Hz, 1H), 5.04 (ddd, $J = 11.1, 1.5, 1.5$ Hz, 1H), 3.95–3.88 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.44–2.41 (m, 1H), 2.34–2.30 (m, 1H), 1.65 (br s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.1, 148.1, 138.6, 135.6, 118.4, 117.5, 111.1, 109.6, 55.9, 55.1, 44.4, 38.6; MS (CI) m/z (relative intensity) 208 ($\text{M}+1$, 6%).

(S)-N-(1-(3,4-Dimethoxyphenyl)-but-3-enyl)benzamide (4h). To a solution of

2h (1.92 g, 5.0 mmol) in THF (90 mL) at -78°C was added *n*-BuLi (3.2 mL, 1.6 M

in THF, 5.1 mmol). After 1 h, benzoic anhydride (1.4 g, 6.0 mmol) was added in one portion. The reaction mixture was allowed to warm to ambient temperature over ca.

16 h, then partitioned between water and CH_2Cl_2 . The organic phase was washed with brine and dried over MgSO_4 . Flash chromatography (2:1 $\rightarrow$ 1:1 hexane/ethyl acetate) gave the benzamide as a colorless oil (2.33 g, 96%). To a solution of this oil (1.5 g, 3.09 mmol) in THF/HMPA (20:1, 42 mL) at -78°C was added SmI_2 (90 mL, 0.1 M in THF, 9.0 mmol). After 10 min, the reaction mixture was partitioned between water and CH_2Cl_2 . The organic phase was washed with brine and dried over MgSO_4 . Flash chromatography gave oxazolidinone **3** (0.42 g, 77%) and benzamide **4h** (0.78 g, 81%) as a colorless solid; mp 135–136 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} -27^\circ$ (c 0.13, CHCl_3); IR (film) 3323, 3069, 3002, 2940, 2909, 2832, 1633, 1520, 1462, 1264, 1232, 1142, 1025, 902 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.80–7.70 (m, 2H), 7.50–7.23 (m, 3H), 6.90–6.78 (m, 3H), 6.44 (br d, $J = 7.5$ Hz, 1H), 5.75 (dddd, $J = 17.0, 10.0, 7.0, 7.0$ Hz, 1H), 5.20 (ddd, $J = 7.0, 7.0, 7.0$ Hz, 1H), 5.15 (br d, $J = 17.0$ Hz, 1H), 5.09 (br d, $J = 10.0$ Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.70–2.62 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 149.2, 148.4, 134.7, 134.4, 134.3, 131.5, 128.6, 126.9, 118.4, 118.3, 111.4, 110.5, 56.0, 55.9, 52.7, 40.5; MS (APCI) m/z (relative intensity) 312 ($[\text{M}+1]^+$, 63%); Anal. Calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.36; H, 6.81; N, 4.51.

(S)-N-[1-(3,4-Dimethoxyphenyl)-3-oxo-butyl]-benzamide (8). A mixture of benzamide **4h** (622 mg, 2.0 mmol), PdCl₂ (72 mg, 0.40 mmol) and Cu(OAc)₂ (148 mg, 0.80 mmol) in H₂O/DMF (1:7, 16 mL) was stirred under oxygen (1 atm) for 2 d. To the brownish mixture, was added 1% HCl solution. The resulting clear solution was extracted with CH₂Cl₂. The organic phase was washed with saturated NaHCO₃ solution and brine. It was dried over MgSO₄, concentrated and purified by flash chromatography (1:1 hexane-EtOAc). Methyl ketone **8** was obtained as a colorless solid (576 mg, 88%). mp 139–140 °C; [α]_D²¹ –9.5° (*c* 0.39, CHCl₃); IR (film) 3329, 3064, 2997, 2940, 2837, 1715, 1636, 1516, 1462, 1418, 1359, 1261, 1142, 1026 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.50–7.40 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.88–6.80 (m, 3H), 5.55–5.49 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.20 (d, *J* = 16.5 Hz, 1H), 3.00 (d, *J* = 16.5 Hz, 1H), 2.13 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 208.1, 166.6, 149.3, 148.1, 134.3, 133.6, 131.6, 128.6, 127.0, 118.4, 111.4, 110.4, 56.0, 55.9, 50.0, 48.1, 31.0; MS (APCI) *m/z* (relative intensity) 327 ([M+1]⁺, 46%); Anal. Calcd. for C₁₉H₂₁NO₄: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.51; H, 6.36; N, 4.17.

(S)-N-[1-(3,4-Dimethoxyphenyl)-3-oxo-butyl]-2,2,2-trifluoroacetamide (9). Using the procedure for preparation of **8**, from trifluoroacetamide *rac*-**6h** (45 mg, 0.14 mmol), PdCl₂ (6 mg, 0.03 mmol) and Cu(OAc)₂ (19 mg, 0.09 mmol) was obtained methyl ketone **9** (33 mg, 71%) as a colorless solid; mp 94.0–94.5 °C; IR (KBr) 3086, 2943, 2352, 2330, 1721, 1700, 1595, 1565, 1526, 1260, 1191, 1160, 1026 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (br d, *J* = 7.9 Hz, 1H), 6.84–6.78 (m, 3H), 5.34–5.27 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.18 (dd, *J* = 17.2, 5.3 Hz, 1H), 2.97 (dd, *J* = 17.2, 6.1 Hz, 1H), 2.12 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 207.1, 156.5 (²*J*_{CF} = 36.9 Hz), 149.2, 148.9, 131.6, 118.4, 115.7 (¹*J*_{CF} = 286 Hz), 111.4, 110.0, 55.9 (2C), 50.1, 47.0, 30.8; MS (EI) *m/z* (relative intensity) 319.16 ([M]⁺, 26%); Anal. Calcd. for C₁₄H₁₆F₃NO₄: C, 52.67; H, 5.05; N, 4.39. Found: C, 52.57; H, 4.91; N, 4.33.

(S)-Benzyl-[1-(3,4-dimethoxy-phenyl)-but-3-enyl]amine (10). To a solution of benzamide **4h** (227 mg, 0.73 mmol) in THF (7.0 mL) was added LiAlH₄ (1.0 M in Et₂O, 3.0 mL, 3.0 mmol). The mixture was heated at reflux for 20 h, after which the mixture was cloudy white, then was quenched by saturated NH₄Cl solution. The resulting slurry was diluted with EtOAc and filtered with the aid of additional EtOAc. The filtrate was dried over MgSO₄, concentrated and purified by flash chromatography (2:1 Hexane- EtOAc) to give the benzylamine **10** (152 mg, 70%) as a colorless oil; [α]_D²⁵ –55° (*c* 1.0, CHCl₃); IR (film) 3323, 3067, 2999, 2933, 2833, 1638, 1592, 1514, 1463, 1418, 1359, 1263, 1234, 1157, 1140, 1029, 916 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.30–7.14 (m, 5H), 6.93 (d, *J* = 1.7 Hz, 1H), 6.86–6.78 (m, 2H), 5.80–5.65 (m, 1H), 5.08–5.01 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.68–3.50 (m, 3H), 2.42–2.35 (m, 2H), 1.75 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 149.2, 148.1, 140.7, 136.5, 135.6, 128.4, 128.2, 126.9, 119.6, 117.5, 111.1, 110.2, 61.4, 55.9 (2C), 51.5, 43.3; MS (MALDI) *m/z* (relative intensity) 298 ([M+1]⁺, 63%); Anal. Calcd. for C₁₉H₂₃NO₂: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.48; H, 7.79; N, 4.70.

Cross metathesis (General Procedure F). To a Schlenk tube containing *rac*-**6a** or *rac*-**6h** (0.164 mmol) and a stirring bar, was added CH₂Cl₂ (2.7 mL) and the appropriate alkene (3 equiv) under argon. Second generation Grubbs catalyst **21a** (5% mol) was then added in one portion under argon. With a stream of argon applied through the sidearm of the Schlenk tube, the pink solution was heated to reflux and monitored by TLC. Upon completion of the reaction (typically 3 h), the mixture was concentrated and filtered through a short plug of silica gel, eluting with EtOAc. Concentration and purification by flash chromatography gave the cross metathesis products **11–15** and **17–18**.

(E)-2,2,2-Trifluoro-N-(1-phenyl-4-trimethylsilyl-but-3-enyl)-acetamide (11).

From *rac*-**6a** (40 mg, 0.164 mmol) and allyltrimethylsilane (80 μ L, 0.492 mmol) by General Procedure F was obtained a colorless oil (43 mg, 80%, *E/Z* = 2:1). Further chromatography (20:1 petroleum ether-methyl *t*-butyl ether) gave **11** as a colorless oil; IR (film) 3309, 3085, 3036, 2947, 2907, 1715, 1698, 1653, 1557, 1539, 1453, 1416, 1317, 1248, 1183 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.22 (m, 5H), 6.47 (br s, 1H), 5.53 (ddd, J = 16.2, 8.1, 8.1 Hz, 1H), 5.10-5.05 (m, 1H), 4.98 (ddd, J = 7.0, 7.0, 7.0 Hz, 1H), 2.60-2.55 (m, 2H), 1.41 (d, J = 8.1 Hz, 1H), -0.06 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.4 ($^2J_{\text{CF}}$ = 36.9 Hz), 139.6, 132.1, 128.9, 128.0, 126.4, 122.0, 115.9 ($^1J_{\text{CF}}$ = 286.4 Hz), 53.8, 39.1, 23.1, -2.1; MS (MALDI) m/z (relative intensity) 330 ($[\text{M}+1]^+$, 8%); HRMS-Cl (m/z) $[\text{M}+1]^+$ calcd. for $\text{C}_{16}\text{H}_{23}\text{F}_3\text{NOSi}$, 330.1501; found, 330.1500.

(E)-2,2,2-Trifluoro-N-(8-hydroxy-1-phenyl-oct-3-enyl)-acetamide (12).

From *rac*-**6a** (40 mg, 0.164 mmol) and 5-hexen-1-ol (57 μ L, 0.492 mmol) by General Procedure F was obtained a colorless oil (35 mg, 68%, *E/Z* = 7:1). Further chromatography (1:1 petroleum ether-methyl *t*-butyl ether) gave **12** as a colorless oil; IR (film) 3296, 3071, 3036, 2935, 2862, 1700, 1653, 1558, 1537, 1456, 1369, 1208, 1185, 1159, 1056 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.23 (m, 5H), 6.52 (br s, 1H), 5.54 (ddd, J = 15.2, 6.8, 6.8 Hz, 1H), 5.31-5.26 (m, 1H), 5.01 (ddd, J = 7.0, 7.0, 7.0 Hz, 1H), 3.59 (dd, J = 6.4, 6.4 Hz, 2H), 2.59-2.55 (m, 2H), 2.01-1.97 (m, 2H), 1.50-1.38 (m, 4H), 1.21 (br s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.4 ($^2J_{\text{CF}}$ = 36.9 Hz), 139.6, 135.2, 128.8, 127.9, 126.3, 124.4, 115.9 ($^1J_{\text{CF}}$ = 286.6 Hz), 62.5, 53.5, 38.7, 32.1, 32.0, 25.2; MS (MALDI) m/z (relative intensity) 316 ($[\text{M}+1]^+$, 23%); Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NO}_2$: C, 60.94; H, 6.39; N, 4.44. Found: C, 60.95; H, 6.45; N, 4.27.

5-Phenyl-5-(2,2,2-trifluoro-acetyl-amino)-pent-2-enoic acid methyl ester (13).

From *rac*-**6h** (40 mg, 0.164 mmol) and methyl acrylate (45 μ L, 0.492 mmol) by General Procedure F was obtained **13** (45 mg, 86%, *E/Z* = 4.5:1) as a colorless solid; mp 87–88 $^{\circ}\text{C}$; IR (film) 3307, 3090, 3038, 2950, 1701, 1651, 1556, 1542, 1438, 1281, 1204, 1178, 1036 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.25 (m, 5H), 6.76 (ddd, J = 16.0, 7.5, 7.5 Hz, 1H), 6.69 (br d, J = 6.0 Hz, 1H), 5.86 (dddd, J = 16.0, 1.5, 1.5, 1.5 Hz, 1H), 5.12 (ddd, J = 7.5, 7.5, 7.5 Hz, 1H), 3.68 (s, 3H), 2.85-2.76 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.9, 166.2, 156.6 ($^2J_{\text{CF}}$ = 36.9 Hz), 142.6, 138.6, 129.3, 128.6, 126.5, 124.7, 115.8 ($^1J_{\text{CF}}$ = 286.5 Hz), 53.2, 51.6, 37.8; Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NO}_3$: C, 55.82; H, 4.68; N, 4.65. Found: C, 55.98; H, 4.62; N, 4.72.

(E)-2,2,2-Trifluoro-N-(7-oxo-1-phenyl-3-oct-enyl)-acetamide (14).

From *rac*-**6a** (40 mg, 0.164 mmol) and 5-hexen-2-one (59 μ L, 0.492 mmol) by General Procedure F was obtained a colorless oil (37 mg, 72%, *E/Z* = 4.5:1). Further chromatography (1:1 hexane-diethyl ether) gave (*E*)-**14** as a colorless solid; (*E*)-**14**: mp 49–50 $^{\circ}\text{C}$; IR (film) 3348, 3080, 3028, 2925, 2852, 1715, 1698, 1648, 1542, 1439, 1364, 1222, 1181, 1156 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.23 (m, 5H), 6.69 (m, 1H), 5.51 (ddd, J = 15.0, 6.7, 6.7 Hz, 1H), 5.32-5.26 (m, 1H), 5.03 (dd, J = 7.6, 6.8 Hz, 1H), 2.55-2.52 (m, 2H), 2.49-2.38 (m, 2H), 2.25-2.21 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 207.9, 156.4 ($^2J_{\text{CF}}$ = 36.9 Hz), 139.5, 133.6, 128.8, 127.9, 126.3, 125.1, 115.9 ($^1J_{\text{CF}}$ = 286.4 Hz), 53.3, 42.7, 38.6, 29.8, 26.5; MS (MALDI) m/z (relative intensity) 314 ($[\text{M}+1]^+$, 31%); Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{NO}_2$: C, 61.33; H, 5.79; N, 4.47. Found: C, 61.54; H, 5.88; N, 4.36. (*Z*)-**14**: Colorless oil; IR (film) 3308, 3080, 3007, 2919, 1715, 1701, 1651, 1557, 1540, 1455, 1364, 1204, 1204, 1180, 1157 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.27 (m, 6H), 5.41-5.28 (m, 2H), 5.03 (ddd, J = 8.7, 5.8, 5.8 Hz, 1H), 2.96-2.89 (m, 1H), 2.63-2.46 (m, 4H), 2.12 (s, 3H), 2.07-2.02 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.2, 156.6 ($^2J_{\text{CF}}$ = 36.9 Hz), 140.7, 131.5, 128.8, 127.8, 126.3, 125.8, 115.7 ($^1J_{\text{CF}}$ = 286.4 Hz), 53.9, 42.5, 33.8, 30.0, 21.2.

(E)-2,2,2-Trifluoro-N-(5-hydroxy-1-phenyl-3-oct-enyl)-acetamide (15). From *rac*-**6a** (40 mg, 0.164 mmol) and *rac*-1-hepten-3-ol (**16**, 60 μ L, 0.492 mmol) by General Procedure F was obtained diastereomeric mixture (*E*)-**15** (32 mg, 61%, dr 3:2 by ^{13}C NMR) as a colorless oil. IR (film) 3334, 3080, 3033, 2961, 2925, 2873, 1694, 1542, 1456, 1248, 1177, 1075, 1023, 1000 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.24 (m, 5H), 6.46 (br s, 1H), 5.61-5.46 (m, 2H), 5.05 (ddd, $J = 7.5, 7.5, 7.5$ Hz, 1H), 4.03 (dd, $J = 6.0, 6.0$ Hz, 1H), 2.67-2.58 (m, 2H), 1.50-1.15 (m, 5H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.5 ($^2J_{\text{CF}} = 36.9$ Hz), 139.4 (major), 139.3 (minor), 137.9, 128.9, 128.1, 126.4, 125.1, 125.0, 115.8 ($^1J_{\text{CF}} = 286.6$ Hz), 72.15 (major), 72.10 (minor), 53.5, 39.28 (major), 39.25 (minor), 38.34 (major), 38.31 (minor), 18.5, 13.8; MS (EI) m/z (relative intensity) 297 ($[\text{M}-\text{H}_2\text{O}]^+$, 9%).

(E)-5-(3,4-Dimethoxy-phenyl)-5-(2,2,2-trifluoro-acetyl-amino)-pent-2-enoic acid methyl ester (17). From *rac*-**6h** (50 mg, 0.164 mmol) and methyl acrylate (45 μ L, 0.492 mmol) by General Procedure F was obtained a colorless oil (58 mg, 98%, *E/Z* = 5:1). Further chromatography gave (*E*)-**17** and (*Z*)-**17** as colorless oils. (*E*)-**17**: IR (film) 3302, 3080, 3007, 2950, 2842, 1718, 1699, 1651, 1555, 1542, 1519, 1460, 1436, 1426, 1263, 1209, 1178, 1160, 1026 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.88 (br d, $J = 6.0$ Hz, 1H), 6.81 (s, 2H), 6.78-6.71 (m, 2H), 5.84 (d, $J = 15.5$ Hz, 1H), 5.03 (dd, $J = 15.0, 7.5$ Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.66 (s, 3H), 2.85-2.71 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.3, 156.5 ($^2J_{\text{CF}} = 36.8$ Hz), 149.4, 149.2, 142.9, 131.1, 124.3, 118.7, 115.8 ($^1J_{\text{CF}} = 286.5$ Hz), 111.6, 110.3, 55.94, 55.90, 52.97, 51.5, 37.5; MS (MALDI) m/z (relative intensity) 362 ($[\text{M}+1]^+$, 7%); HRMS-CI (m/z) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{NO}_5\text{Na}$, 384.1035; found, 384.1032; Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{NO}_5$: C, 53.19; H, 5.02; N, 3.88. Found: C, 53.41; H, 4.94; N, 3.85. (*Z*)-**17**: Colorless oil; IR (film) 3306, 3080, 3007, 2945, 2832, 1717, 1702, 1650, 1557, 1540, 1519, 1454, 1440, 1258, 1209, 1178, 1163, 1026 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.85 (br d, $J = 6.5$ Hz, 1H), 6.90-6.82 (m, 3H), 6.28-6.22 (m, 1H), 6.00 (d, $J = 11.0$ Hz, 1H), 5.02-4.95 (m, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 3.45-3.37 (m, 1H), 2.76-2.68 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.9, 156.8 ($^2J_{\text{CF}} = 36.8$ Hz), 149.3, 148.9, 143.9, 132.7, 123.1, 118.4, 115.8 ($^1J_{\text{CF}} = 286.4$ Hz), 111.5, 109.8, 55.95, 55.93, 53.3, 51.7, 34.9.

N-[9-(*tert*-Butyl-dimethyl-silanyloxy)-1-(3,4-dimethoxy-phenyl)-5-hydroxy-3-enyl]-2,2,2-trifluoro-acetamide (18). From *rac*-**6h** (40 mg, 0.164 mmol) and 7-(*tert*-butyl-dimethyl-silanyloxy)-1-hepten-3-ol⁶⁷ (**19**, 120 mg, 0.492 mmol) by General Procedure F was obtained **18** (25 mg, 30%, *E/Z* = >20:1) as a colorless oil; IR (film) 3347, 3250, 3080, 2933, 2859, 1697, 1517, 1458, 1256, 1153, 1022 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.85-6.79 (m, 2H), 6.76 (s, 1H), 6.40 (br d, $J = 8.5$ Hz, 1H), 5.62-5.48 (m, 2H), 4.99 (ddd, $J = 7.5, 7.5, 7.5$ Hz, 1H), 4.03 (br s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.61-3.55 (m, 4H), 3.58 (t, $J = 6.5$ Hz, 2H), 2.61 (t, $J = 6.5$ Hz, 2H), 1.56-1.43 (m, 7H), 0.87 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3 ($^2J_{\text{CF}} = 37.6$ Hz), 149.3, 137.7, 133.7, 131.9, 125.1, 118.5, 115.8 ($^1J_{\text{CF}} = 287.5$ Hz), 111.5, 110.2, 72.3, 63.0, 56.05, 56.00, 53.4, 38.2, 36.9, 32.6, 25.9, 21.6, 18.2; HRMS-EI (m/z) $[\text{M}]^+$ calcd. for $\text{C}_{25}\text{H}_{40}\text{F}_3\text{NO}_5\text{Si}$, 519.2639; found, 519.2636.

(S)-2,2,2-Trifluoro-N-allyl-N-(1-(3,4-dimethoxyphenyl)-1-butenyl)acetamide (20). To a solution of trifluoroacetamide *rac*-**6h** (53 mg, 0.175 mmol) in THF (1 mL) was added lithium hexamethyldisilazide (0.18 mL, 1 M in THF, 0.87 mmol) and allyl iodide (0.02 mL, 0.2 mmol). Monitoring by TLC showed no reaction. Additional allyl iodide (0.2 mL, 2 mmol) and HMPA (0.1 mL) were added at ambient temperature, and the mixture was stirred in the dark for 16 h. Concentration and flash chromatography gave *N*-allyl product **20** (35 mg, 58%) as a colorless liquid followed by unreacted **6h** (17 mg, 32%). Complicated NMR spectra

were observed for **20** as a result of hindered rotation. IR (film) 3056, 2982, 2939, 2834, 2300, 1686, 1604, 1521, 1477, 1265, 1208, 1152 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.92–6.80 (m, 3H), 5.79–5.66 (m, 2.5H), 5.60–5.48 (m, 4.5H), 3.93–3.67 (m, 8H), 2.93–2.61 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.4 ($^2J_{\text{CF}} = 35.3$ Hz), 149.1, 134.2, 134.0, 133.1, 132.2, 129.8, 128.8, 120.7, 120.1, 118.8, 118.0, 117.8, 116.6 ($^1J_{\text{CF}} = 287$ Hz), 112.0, 111.5, 110.8, 110.7, 59.5, 59.4, 55.9, 55.8, 47.3, 46.1, 35.9, 35.2; MS (EI) m/z (relative intensity) 343.01 ($[\text{M}]^+$, 14%); Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{F}_3\text{NO}_3$: C, 59.47; H, 5.87; N, 4.08. Found: C, 59.49; H, 5.90; N, 4.03.

(S)-2-(3,4-Dimethoxyphenyl)-N-2,2,2-trifluoroacetyl-1,2,3,6-tetrahydropyridine (22).

To a solution of *N*-allyltrifluoroacetamide **20** (25 mg, 0.072 mmol) in CH_2Cl_2 (36 mL) was added Grubbs catalyst **21b** (5.9 mg, 0.0072 mmol). After 16 h at ambient temperature, concentration and flash chromatography gave **22** (21 mg, 92.5%) as a colorless liquid. Complicated NMR spectra were observed for **22** as a result of hindered rotation (two rotamers, ratio 3:2). IR (Film) 2929, 2851, 1687, 1518, 1451, 1257, 1188, 1143, 1027 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.90–6.78 (m, 3H), 6.06–5.90 (m, 1H), 5.98 (d, $J = 6.6$ Hz, 0.6H), 5.66–5.61 (m, 1H), 5.30 (d, $J = 5.7$ Hz, 0.4H), 4.61 (br d, $J = 18.1$ Hz, 0.4H), 4.14 (br d, $J = 17.8$ Hz, 0.6H), 3.86 (s, 3H), 3.83 (s, 3H), 3.56–3.49 (m, 0.6H), 3.24 (br d, $J = 18.9$ Hz, 0.4H), 2.78–2.65 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 156.2 ($^2J_{\text{CF}} = 35.3$ Hz), 155.7 ($J = 35.5$ Hz), 149.1, 148.8, 130.6, 129.8, 124.7, 123.9, 123.4, 122.7, 119.5, 119.2, 116.7 ($^1J_{\text{CF}} = 286$ Hz), 111.0, 110.9, 110.1, 56.0, 55.9, 53.5, 50.1, 40.9, 39.7, 28.2, 26.9; MS (EI) m/z (relative intensity) 315.2 ($[\text{M}]^+$, 42%); Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{NO}_3$: C, 57.14; H, 5.12; N, 4.44. Found: C, 57.32; H, 5.09; N, 4.40.

- i ($\text{R}^1 = \text{TBS}$, $\text{R}^2 = \text{H}$)
 ii ($\text{R}^1 = \text{TBS}$, $\text{R}^2 = \text{CO}_2\text{Me}$)
 iii ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Me}$)
23 ($\text{R}^1 = \text{Ts}$, $\text{R}^2 = \text{CO}_2\text{Me}$)

Toluene-4-sulfonic acid 5-methoxycarbonyloxy-hept-6-enyl ester (23).

To a solution of **i**^{6,7} (1.61 g, 6.59 mmol), pyridine (6 mL) and DMAP (ca. 5 mg) in CH_2Cl_2 (20 mL) at 0 °C was added methyl chloroformate (0.8 mL, 10 mmol). The mixture was allowed to warm to ambient temperature over ca. 16 h, then partitioned between saturated NH_4Cl solution and Et_2O . The organic phase was washed with 2 M HCl, water, and brine, then dried (MgSO_4). Concentration and flash chromatography (hexane/ Et_2O 2:1) gave the carbonate **ii** (1.52 g, 72%) as a pale yellow oil. To a solution of **ii** in THF (11 mL) was added TBAF (6.5 mL, 1.0 M in THF, 6.5 mmol). After ca. 16 h, concentration and flash chromatography (hexane/ Et_2O 1:2) gave the primary alcohol **iii** (0.79 g, 84%) as a pale yellow oil. To a solution of **iii** (445 mg, 2.36 mmol), DMAP (ca. 5 mg) and Et_3N (0.60 mL, 4.3 mmol) in CH_2Cl_2 at 0 °C was added a solution of *p*-toluenesulfonyl chloride (680 mg, 3.53 mmol) in CH_2Cl_2 (18 mL). The clear solution was allowed to warm to ambient temperature in 22 h, then partitioned between water and CH_2Cl_2 . The organic phase was washed with saturated NaHCO_3 solution, 1 M HCl, and brine, then dried (MgSO_4). Concentration and flash chromatography furnished tosylate **23** (686 mg, 85%) as a colorless oil. IR (film): 2956, 2870, 1747, 1598, 1443, 1359, 1266, 1176, 1097 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 5.71 (ddd, $J = 17.5$, 10.5, 7.0 Hz, 1H), 5.23 (ddd, $J = 17.5$, 1.0, 1.0 Hz, 1H), 5.16 (ddd, $J = 10.0$, 1.0, 1.0 Hz, 1H), 4.96 (ddd, $J = 7.0$, 7.0, 7.0 Hz, 1H), 3.98 (dd, $J = 6.0$, 6.0 Hz, 2H), 3.73 (s, 3H), 2.41 (s, 3H), 1.73–1.26 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.2, 144.7, 135.6, 133.3, 129.9, 127.9, 117.7, 78.6, 70.1, 54.6, 33.5, 28.6, 21.6, 21.0; Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_6\text{S}$: C, 56.12; H, 6.48. Found: C, 56.33; H, 6.50.

7-((S)-1-(3,4-Dimethoxyphenyl)but-3-enylamino)hept-1-en-3-yl methyl carbonate (24). To a solution of amine **7** (187 mg, 0.903 mmol), tosylate **23** (257 mg, 0.750 mmol) and Et_3N (0.11 mL, 0.825 mmol) in acetonitrile (9.0 mL), was added sodium iodide (169 mg, 1.12 mmol) in one portion under argon. The

resulting white suspension was heated at reflux for 4 d. Basic brine (2 M NaOH saturated with NaCl) was added to the cooled reaction mixture and the mixture was extracted with CH_2Cl_2 and dried over MgSO_4 . Concentration and flash chromatography (1:1 Hexane-EtOAc to 30:1 CH_2Cl_2 -MeOH to 5:1 CH_2Cl_2 -MeOH) afforded unreacted amine **7** (48 mg) and **24** (183 mg, 65%, dr 1:1) as a pale yellow oil; IR (film) 3427, 3243, 3049, 2985, 2929, 1724, 1652, 1537, 1483, 1455, 1385, 1355, 1334, 1150, 907 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.86 (s, 1H), 6.80-6.77 (m, 2H), 5.77-5.63 (m, 2H), 5.23 (d, $J = 17.0$ Hz, 1H), 5.15 (d, $J = 10.5$ Hz, 1H), 5.09-4.96 (m, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 3.53 (dd, $J = 7.5, 6.0$ Hz, 1H), 2.44-2.27 (m, 4H), 1.68-1.22 (m, 8H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.3, 149.1, 148.0, 136.8, 136.0, 135.6, 119.4, 117.4 (2C), 111.0, 110.0, 79.0, 78.97, 62.4, 55.9, 54.6, 47.4, 43.2, 34.1, 29.9, 22.7; Anal. Calcd. for $\text{C}_{21}\text{H}_{31}\text{NO}_5$: C, 66.82; H, 8.28; N, 3.71. Found: C, 66.82; H, 8.26; N, 3.91.

(R)-1-((S)-1-(3,4-Dimethoxyphenyl)but-3-enyl)-2-vinylpiperidine (2R-25) and (S)-1-((S)-1-(3,4-dimethoxyphenyl)but-3-enyl)-2-vinylpiperidine (2S-25). To a solution of amine **24** (dr 1:1, 84.0 mg, 0.22 mmol), triphenylphosphine (35 mg, 0.13 mmol) and allylpalladium chloride dimer (13 mg, 0.036 mmol), was added Et_3N (80 μL , 0.57 mmol). The resulting solution

was stirred at ambient temperature for 3 d, then concentrated. The residue was taken up by 3:1 hexane-EtOAc and filtered, concentrated and purified by flash chromatography (5:1 to 1:1 Hexane-EtOAc) to give **25** (60 mg, 89%, (2R):(2S) = 1.6:1) as a pale yellow oil. The mixture was used in the next step without separation. Pure diastereomers were obtained by further flash chromatography. (2R)-**25**: pale yellow oil; $[\alpha]_{\text{D}}^{22} +1.2^\circ$ (c 0.6, CHCl_3); IR (film) 3074, 2931, 2851, 2795, 1639, 1590, 1514, 1463, 1416, 1322, 1255, 1235, 1145, 1030 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.95 (s, 1H), 6.89-6.75 (m, 2H), 5.93 (ddd, $J = 18.0, 9.5, 9.5$ Hz, 1H), 5.65 (dddd, $J = 17.0, 10.0, 6.5, 6.5$ Hz, 1H), 5.21 (d, $J = 17.5$ Hz, 1H), 5.10 (d, $J = 10.0$ Hz, 1H), 4.98 (dd, $J = 17.0, 1.5$ Hz, 1H), 4.90 (d, $J = 10.0$ Hz, 1H), 3.96-3.90 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.19 (dd, $J = 6.5, 6.5$ Hz, 1H), 2.63-2.41 (m, 3H), 2.16 (dd, $J = 10.0, 10.0$ Hz, 1H), 1.80-1.15 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 148.6, 147.7, 141.6, 137.0, 135.2, 120.7, 115.9, 115.4, 112.6, 110.4, 62.8, 62.7, 55.92, 55.87, 45.2, 34.0, 30.4, 26.2, 23.7; MS (APCI) m/z (relative intensity) 302 ($[\text{M}+1]^+$, 48%); Anal. Calcd. for $\text{C}_{19}\text{H}_{27}\text{NO}_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.84; H, 9.17; N, 4.34. (2S)-**25**: pale yellow oil; $[\alpha]_{\text{D}}^{22} +20^\circ$ (c 0.15, CHCl_3); IR (film) 3073, 2931, 2835, 2801, 2713, 1734, 1640, 1589, 1514, 1463, 1418, 1261, 1146, 1029 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.85-6.70 (m, 3H), 5.88 (ddd, $J = 17.5, 8.5, 8.5$ Hz, 1H), 5.74 (dddd, $J = 17.0, 10.5, 7.0, 7.0$ Hz, 1H), 5.19-5.11 (m, 2H), 4.98 (dd, $J = 17.0, 1.5$ Hz, 1H), 4.94-4.88 (m, 1H), 3.98 (dd, $J = 7.5, 7.5$ Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.93-2.84 (m, 1H), 2.72-2.46 (m, 2H), 1.85-1.02 (m, 8H); ^{13}C NMR (125 MHz, CDCl_3) δ 148.1, 147.7, 143.8, 136.9, 130.3, 121.1, 115.5, 115.1, 112.9, 110.4, 63.7, 62.7, 55.9, 55.8, 45.5, 37.2, 34.8, 26.3, 24.1; MS (MALDI) m/z (relative intensity) 302 ($[\text{M}+1]^+$, 27%); HRMS-Cl (m/z) $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{19}\text{H}_{28}\text{NO}_2$, 302.2107; found, 302.2112.

(1S,2S)-6-(3,4-Dimethoxy-phenyl)-1,3,4,6,7,9a-hexahydro-2H-quinolizine (26). A diastereomeric mixture of 2-vinylpiperidines (2R)-**25** and (2S)-**25** (114 mg, 0.378 mmol, dr = 1:1) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (78 mg, 0.40 mmol) in CH_2Cl_2 (170 mL) was stirred at ambient temperature for 3 h. Second generation Grubbs catalyst **21b** (50 mg, 0.0588 mmol) was added in one

portion under argon. After 2 d at ambient temperature, a second portion of **21b** (20 mg, 0.024 mmol) was added. After another 36 h, the mixture was concentrated, acidified with 2 M HCl, and washed with EtOAc to remove the catalyst. The acidic aqueous phase was adjusted to pH 10 (2 M NaOH), extracted with CH_2Cl_2 , and concentrated to afford **26** as a diastereomeric mixture (dr 1:1). Flash chromatography

(2:1 Hexane-EtOAc to 20:1 EtOAc-MeOH to 8:1 EtOAc-MeOH) furnished the two separated diastereomers (88 mg in total, 85%) (9a*R*)-**26** and (9a*S*)-**26**. (9a*R*)-**26**: pale yellow oil; $[\alpha]_D^{25}$ -60° (*c* 0.8, CHCl₃); IR (film) 2927, 2850, 2739, 1589, 1511, 1460, 1323, 1260, 1144, 1029 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.86 (s, 1H), 6.82-6.74 (m, 2H), 5.90-5.84 (m, 1H), 5.57 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.88-2.79 (m, 1H), 2.72 (d, *J* = 11.5 Hz, 1H), 2.66 (d, *J* = 11.0 Hz, 1H), 2.26 (dd, *J* = 18.0, 1.5 Hz, 1H), 2.12-1.08 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 148.5, 148.1, 138.4, 130.9, 124.2, 121.1, 111.8, 110.4, 61.0, 55.88, 55.82, 54.6, 52.5, 32.2, 31.9, 25.3, 24.7; HRMS-EI (*m/z*) [*M*]⁺ calcd. for C₁₇H₂₃NO₂, 273.1729; found, 273.1724. (9a*S*)-**26**: pale yellow oil; $[\alpha]_D^{25}$ -58° (*c* 0.42, CHCl₃); IR (film) 2930, 2878, 2783 and 2728 (Bohlmann bands), 1698, 1648, 1516, 1260, 1233, 1134, 1029 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.88 (s, 1H), 6.83-6.75 (m, 2H), 5.76-5.69 (m, 1H), 5.88 (d, *J* = 9.5 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.22 (dd, *J* = 10.5, 3.5 Hz, 1H), 2.67 (d, *J* = 11.0 Hz, 2H), 2.45-2.38 (m, 1H), 2.25-1.15 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 149.3, 148.1, 136.3, 130.7, 124.6, 120.4, 110.8, 110.6, 66.1, 63.21, 56.1, 55.9, 52.5, 36.5, 32.7, 26.3, 25.1; MS (APCI) *m/z* (relative intensity) 274 ([*M*+1]⁺, 100%); HRMS-ESI (*m/z*) [*M*+H]⁺ calcd. for C₁₇H₂₄NO₂, 274.1807; found, 274.1804.

Stereochemical Assignments

(a) Chemical correlation of **2a**.

(S)-N-1-Phenyl-but-3-enyl-benzamide (4). To a solution of **2a** (70 mg, 0.217 mmol) in THF (2.5 mL) at -78°C was added *n*-BuLi (0.18 mL, 2.5 M in THF, 0.45 mmol). After 1 h, benzoic anhydride (102 mg, 0.434 mmol) was added in one portion. The reaction mixture was allowed to warm to r.t. overnight, then partitioned between water and CH₂Cl₂. The organic phase was washed with brine and dried over MgSO₄. Flash chromatography gave a colorless oil (75 mg, 81%). To a solution of this oil (75 mg) in THF/HMPA (20:1, 2.3 mL) at -78°C was added SmI₂ (10 mL, 0.1 M in THF, 1.0 mmol). After 10 min, the reaction mixture was partitioned between water and CH₂Cl₂. The organic phase was washed with brine and dried over MgSO₄. Flash chromatography gave **4** (41 mg, 93%) as a colorless solid. mp 98–99 °C; $[\alpha]_D^{20}$ -20° (*c* 0.34, CHCl₃); spectroscopic data matched those from the literature,⁸ and those of an authentic sample prepared as described below. The oxazolidinone **3** was recovered (30 mg, 96%).

An authentic sample of **4** was prepared by benzoylation of the known homoallylic amine.⁹ Thus, to a solution of the homoallylic amine (0.38 mmol) in CH₂Cl₂ (2 mL) under ice-bath, was added pyridine (0.38 mmol) and benzoyl chloride (0.45 mmol). After 1 h, water (2 mL) was added and the organic phase was washed with 2 N HCl, 10% NaOH and brine. Then it was dried over MgSO₄, concentrated and purified by flash chromatography to give **4** as a colorless solid. 99–101 °C; $[\alpha]_D^{20}$ -22° (*c* 0.34, CHCl₃); IR (film) 3334, 3064, 3030, 2916, 1634, 1592, 1491, 1304, 1073, 921 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.80-7.35 (m, 10H), 6.42 (d, *J* = 6.8 Hz, 1H), 5.76 (dddd, *J* = 17.1, 10.1, 6.7, 6.7 Hz, 1H), 5.30 (ddd, apparent q, *J* = 7.1 Hz, 1H), 5.17 (ddd, *J* = 17.1, 1.0, 0.9 Hz, 1H), 5.12 (ddd, *J* = 10.1, 0.9, 0.9 Hz, 1H), 2.69 (dd, apparent t, *J* = 6.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.8, 141.8, 134.7, 134.2, 131.5, 128.7, 128.6, 127.4, 127.0, 126.5, 118.4, 52.9, 40.6; MS (EI) *m/z* (relative intensity) 251([*M*+H]⁺, 42%).

(b) Chemical correlation of 2g.

A mixture of **2g** (9 mg, 0.033 mmol) and 20% Pd(OH)₂ on carbon (10 mg) in methanol (0.5 mL) was stirred overnight under H₂ (1 atm). Filtration and concentration gave **5** (10 mg, 100%) as a colorless oil; ¹H NMR and TLC data and HPLC retention times for both major and minor diastereomers were identical to an authentic sample produced by *n*-propyl radical addition to **1g** (previously shown to furnish predominantly products of *Si*-face attack).¹⁰

(c) Assignment of cross-metathesis isomers.

For major isomers obtained in cross-metathesis, the *E* configuration was assigned by ¹H NMR spectroscopy and literature precedent according to the following analyses. (a) Large coupling constants (15–16 Hz) were observed for the olefinic hydrogens in the major isomers of **11–15** and **17**. For **17**, the major and minor isomers had *J* = 16 and 11 Hz, respectively, confirming that the 16 Hz coupling was associated with (*E*)-**17**. (b) Furthermore, all *Z*-isomers had clearly resolved resonances for the geminal protons of the allylic CH₂, while the *E*-isomers offered little or no resolution of those protons. This assignment was supported by correlation to literature data¹¹ on related compounds **E** and **F** (shown at right); the anisotropy affecting H^a and H^b was associated with the *Z*-isomer. (c) Using a simplified analog (**G**), conformational analysis (Chem3D) using molecular dynamics followed by energy minimization (MM2) suggested a source of the anisotropy affecting H^a and H^b. One of these protons was clearly localized on the “inside” of the allylic system and proximal to the hydroxyl group. The extended structures of the *E* isomers offer no obvious source of such anisotropy.

H^a, H^b = 2.48–2.65 ppm (multiplet)

H^a, H^b = 2.68 and 2.81 ppm (two resolved multiplets)

For **15** and **18**, prepared using racemic allylic alcohols, four diastereomers could be envisioned. A mixture of two of the four possible diastereomers was obtained; both were assigned *E*-configuration according to the analysis above. The diastereomerism was attributed to the hydroxyl-bearing stereogenic center. The presence of small amounts (<10%) of the *Z* isomers in the crude product mixture was not ruled out.

Effects of Chiral Ligands on Intramolecular Allylic Amination of 24.

The procedure given for preparation of **25** was modified to screen the effects of several chiral ligands: From amine **24** (6.0 mg, 0.027 M in CH₂Cl₂, 0.016 mmol), using (+)-*N,N'*-bis(2'-diphenylphosphino-benzoyl)-1,2-diaminocyclohexane ((1*R*,2*R*)-Trostr ligand, 10 mg, 0.014 mmol), allylpalladium chloride dimer (1.6 mg, 0.0043 mmol) and Et₃N (6 μL, 0.043 mmol) by the above procedure (2 d), was obtained **25** as a pale yellow oil (4.3 mg, 90%, (2*R*):(2*S*) = 1.05:1). From amine **24** (232 mg, 0.036 M in CH₂Cl₂, 0.615 mmol), using (–)-*N,N'*-bis(2'-diphenylphosphino-benzoyl)-1,2-diaminocyclohexane ((1*S*,2*S*)-Trostr ligand, 66 mg, 0.094 mmol), allylpalladium chloride dimer (11.5 mg, 0.031 mmol) and Et₃N (220 μL, 1.57 mmol) by the above procedure (60 h), was obtained **25** as a

pale yellow oil (151 mg, 81%, (2*R*):(2*S*) = 1.1:1). From amine **24** (6.3 mg, 0.027 M in CH₂Cl₂, 0.017 mmol), using (+)-*N,N'*-bis(2'-diphenylphosphino-1-naphthoyl)-1,2-diaminocyclohexane ((1*R*,2*R*)-Trosta ligand (naphthyl), 11 mg, 0.013 mmol), allylpalladium chloride dimer (1.5 mg, 0.0041 mmol) and Et₃N (6 µL, 0.043 mmol) by the above procedure (3 d), was obtained **25** as a pale yellow oil (4.3 mg, 86%, (2*R*):(2*S*) = 1:1).

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S19 (Compound 2b)

S27 (Compound (2S)-25)